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INTERACTION OF NITRILOTRIACETIC ACID WITH SUSPENDED AND BOTTOM MATERIAL

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INTERACTION OF NITRILOTRIACETIC ACID WITH SUSPENDED AND BOTTOM MATERIAL

by

Division of Analytical Chemistry
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

for the

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ABSTRACT

An experimental investigation was made of the possible interaction of residual concentrations of nitrilotriacetic acid in surface waters with metallic elements contained in sediments and bottom materials. Samples of bottom materials from typical bodies of surface waters were analyzed for their major, minor, and trace constituents. Eight representative samples of these were equilibrated with distilled water and with water containing 20 ppm of NTA and the resulting solutions were analyzed by three analytical techniques. Elements showing essentially no increased solubility in the presence of NTA were: barium, antimony, molybdenum, strontium, chromium, silver, tin, iron, lead, cadmium, copper, and mercury. Elements showing small increases in solubility were: nickel, zinc, manganese, and cobalt. Calcium and magnesium concentrations were increased somewhat above their normal relatively high concentrations.

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SECTION I

CONCLUSIONS

The possible interaction of residual concentrations of nitrilotriacetic acid in natural waters with sediments and bottom materials has been investigated. Analysis of the aqueous phase, with and without residual concentrations of NTA, equilibrated with representative bottom materials shows no interaction in a majority of cases and slight interactions in four cases.

Metallic elements that show essentially no increased solubility in the presence of 20 ppm of NTA are: barium, antimony, molybdenum, strontium, chromium, silver, tin, iron, lead, cadmium, copper, and mercury. Elements showing somewhat increased solubility in the presence of residual concentrations NTA are the following: nickel, zinc, manganese, and cobalt. All of the latter elements except calcium and magnesium were present in the ordinary water at sub parts-per-million levels and their concentrations never increased by more than 2 or 3 fold in the presence of NTA. Magnesium and calcium, as expected, were found to be present at the multi parts-per-million level and the small increases caused by the NTA were again considered to be of little practical significance.

SECTION II

RECOMMENDATIONS

The present study indicates that residual concentrations of NTA in surface waters do not markedly increase the solubility of sediments in natural waters. However, the studies were carried out in an empirical manner and no effort was made to understand the complex physicochemical equilibra involved.

A more definitive understanding of NTA interactions is very desirable. Such studies should systematically investigate the effects of variation of concentration, pH, and temperature. The ultimate fate and possible modes of disappearance of NTA by other means than biodegradation need to be investigated. The speciation of selected elements in the aqueous environment - ionic, complex, sediment - should be investigated, particularly as it is influenced by intrusions of complexants such as NTA. Because there is always the possibility that environmental incidents can occur, the effects of massive concentrations of NTA should be studied and threshold limits, if any, should be established.

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SECTION III

INTRODUCTION

Increased eutrophic activity in inland waters attributed, in part, to widespread use of phosphate - containing detergents has stimulated efforts to find substitute builders. One of the more promising of these is nitrilo-triacetic acid. NTA is a more effective chelating agent than sodium tripolyphosphate by a factor of 1.4. Thus, a smaller amount would be required in detergent formulations. While it would substitute another nutrient, nitrogen for phosphorous, the widespread use of NTA would only increase nitrogen levels in waste waters by 3 percent.

Several objections of a different nature have been raised to the use of NTA. It does not readily biodegrade under anaerobic conditions and there is some evidence that NTA facilitates the transport of cadmium and mercury across the placental barrier of test animals with consequent damage to the fetus. It is believed that further research is underway to better understand the nature of these problems.

A further potential problem is concerned with the chelating action of NTA. Because of its slow rate of degradability and its superior chelating action, there is the possibility that significant amounts of NTA would accumulate in bodies of water and interact with insoluble hazardous materials contained in silts and sediments. It was the purpose of the present research to investigate this situation.

The plan of the work was to use a multi-competence semi-quantitative approach to ascertain whether residual amounts of NTA would influence the concentrations of heavy metals in water. For the purpose of this work, a solution containing 20 ppm of NTA was selected as the maximum residual level that could be expected in untreated domestic sewage, if phosphates were completely replaced by NTA. Such a level is, of course, higher than levels expected to occur in bodies of water. Samples of silts and sediments were obtained from typical bodies of surface water and analyzed for their major, minor, and trace constituents. Representative materials were equilibrated with distilled water and water containing 20 ppm of NTA and the resulting solutions were analyzed using atomic absorption spectrometry, isotope-dilution spark-source mass spectrometry, and neutron activation analysis.

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SECTION IV

DESCRIPTION OF SAMPLES

Eighteen samples of bottom material were obtained for these measurements, selected to be representative of a wide variety of silts and sediments. These materials were obtained through the Chief, Contaminants Characterization Program, Southeast Water Laboratory, Athens, Georgia, who in turn solicited the collaboration of colleagues in a number of EPA laboratories throughout the country.

The samples received are listed in Table 1. They were collected by experienced water scientists, and packaged in glass jars or polyethylene bottles with enough water to insure that they were moist when received. These materials were sampled for analysis by a coring technique. A polyethylene tube, approximately one-half inch in diameter was forced into the settled material to provide several core samples which were combined. These were then freeze-dried and the dried material was carefully mixed, prior to analysis. While visual observation indicated non-homogeneity of the samples, it is believed that the procedure followed provided samples that were qualitatively representative of the bulk material.

The samples were analyzed by a semi-quantitative emission spectrochemical procedure which screens for 54 elements. The procedure consisted in mixing 5 mg of the freeze-dried material with high purity graphite and burning this to completion on an under-cut electrode. The samples were excited in an atmosphere of 70 percent argon - 30 percent oxygen to reduce the band structure from CN which would otherwise cover some of the sensitive lines of trace constituents. The results of these analyses are given in Table 2.

Selected samples of the bottom materials were analyzed by a more quantitative spectrographic technique. For this purpose, the freeze-dried material was pulverized and mixed using plastic vials and plexiglas balls. For elements with low boiling points - Cd, Hg - a boiler-cap technique was employed with 50 mg charges excited with an argon - oxygen envelope around the arc and an argon atmosphere in the shielding chamber. These conditions gave low background and limits of detection of 0.005 percent for cadmium and 0.0005 percent for mercury. For the other elements, 10 mg charges were burned to completion at 20 amperes in a dc arc in the same type atmosphere. The results are shown in Table 3.

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Table 1. Catalogue of Bottom Materials Samples

NBS Identification Number	Sample Description
37913	Hudels Basins Office Sample #3 [1]
37914	Hudeis Basins Office Sample #4 [1]
37915	Ohio R. Cincinnati, RM. 486 (8/21/70) [2]
37916	Houston Ship Channel 8.16 μg Hg/g dry wt. T–1 [3]
37917	Miss. R. 44.2 μg Hg/g dry wt. D–6 [3]
37918	Hg 12080 DH 42 1.5' 1091 [4]
37919	13701, 13733, 13735 (Composite) [2]
37920	Coweeta Watershed, N. C. Shope Cr. Unpoll. Sample for Control [5]
37921	Whitehall Watershed, Athens, Ga. Unpoll. Sample for Control [5]
37922	Mobile R. Basin (Caustic Plant Fallout) OM–3 [5]
37923	Tombigbee R., T–3 [5]
37933	Potomac R. Blue Plain Mud Buoy #8 9–2–70 [4]
37934	Coastal Sediment #2 [6]
37935	Miss. R. 2 mi. below CBQRR Bridge Sample LMBO 7168 [7]
37936	Miss. R. 100' off Iowa Shore Sample LMBO 7169 [7]
37947	Coastal Sediment #3, [6]
37950	Yaquina Bay Sample #5 [6]
37961	West Coast Sediment #4, Received 10/6/70 FWQA Alameda, California [6]

Sample Source

[1] Hudson–Delaware Basins Office, Edison, New Jersey
[2] Analytical Quality Control Laboratory, Cincinnati, Ohio
[3] Kerr Water Research Center, Ada, Oklahoma
[4] Middle Atlantic Regional Office, Charlottesville, Virginia
[5] Southeast Water Laboratory, Athens, Georgia
[6] Pacific Northwest Water Laboratory, Corvallis, Oregon
[7] Lake Michigan Basins Office, Chicago, Illinois

Table 2. Emission Spectrographic Analysis of Bottom Materials

NBS Sample Designation	Percent					
	>10	1 – 10	0.1 – 1	0.01 – 0.1	0.001 – 0.01	<0.001
37913	Ca	Ba, Fe, Mg, Na, Si	Al, As, B, Cu, K, P, Sn, Ti	Cr, Mn, Ni, Pb, Zn	Mo	Ag, Be, In, Sn
37914	Ca	Ba, Fe, Mg, Si	Al, As, Cu, K, Na, Sr, Ti	B, Cr, Hg, Mn, Ni, Pb, Zn	Mo	Ag, Be, In, Sn
37915	Si	Al, Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Mn, Ni, Sr, Zr	Cu, Pb	Ag, Bi, In, Mo, Sn
37916	Si	Al, Ca, Fe	Ba, K, Na, P, Ti	B, Cr, Cu, Mn, Ni, Pb, Sr, Zr, Zn		Ag, Be, In, Mo, Sn
37917	Si	Al, Ca, Fe	Ba, K, Na, Ti	B, Cr, Mn, Ni, Sr, Zn, Zr	Cu, Pb	Ag, Be, In, Mo, Sn
37918	Si	Al, Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Mn, Ni, Sr	Cu, Pb	Ag, In, Mo, Sn
37919	Al, Ca, Si	Fe, Mg	Ba, Cu, K, Na, P, Ti	Cr, Mn, Ni, Pb, Sr, Zn	Ag, In	Be, Mo, Sn
37920	Al, Si	Ca, Fe	Ba, K, Mg, Na, Ti	Cr, Mn, Ni, Sr, V, Zr	Cu, Pb	Ag, Be, In, Mo, Sn
37921	Al, Si	Ca, Fe	Ba, K, Mg, Ti	B, Cr, Mn, Na, Ni, Sr, Zr	Cu, Pb	Ag, Be, In, Mo, Sn
37922	Al, Si	Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Hg, Mn, Ni, Sr, V, Zr	Cu, Pb	Ag, Be, In, Mo, Sn
37923	Al, Si	Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Mn, Ni, Sr	Cu, Pb	Ag, Be, In, Mo, Sn
37933	Al, Si	Ca, Fe	Ba, Cu, K, Mg, Na, P, Ti	B, Cr, Mn, Ni, Pb, Sr, Zn	Ag	Be, In, Mo, Sn
37934	Al, Si	Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Cu, Mn, Ni, Pb, Sr, Zn, Zr		Ag, Bi, In, Mo, Sn
37935	Si	Al, Ca, Fe	Ba, K, Mg, Na, Ti	B, Cr, Mn, Ni, Sr, Zn, Zr	Cu, Pb	Ag, Be, In, Sn
37936	Si	Al, Ca, Fe	Ba, K, Mg, Na, Ti	Mn, Sr,	Cu, Pb	Ag, Be, In
37947	Ca, Si	Fe, Mg, Na, Ti	Al, Ba, Cr, Cu, Mn	Ni, Sr,	Co, V	Ag, Mo, Pb, Sn
37950	Ca, Mg, Si	Al, Cr, Fe, Mn, Na, Ti	Ba	Cu, Sr	Co, Ni, Sn, V	Ag, Mo, Pb
37961	Ca, Si	Fe, Mg, Na, Ti	Al, Ba, Cr, Cu, Mn	Ni, Sr	V, Co	Ag, Mo, Pb, Sn

Table 3. Spectrochemical Determination of Selected Elements in Freeze-Dried Sediments

Sample No.	Ag	Be	Bi	Cd	Cr	Cu	Ge	Hg	In	Pb	Sn	V	Zn
NBS 37914	.0005	–	–	–	.05	>.1	–	.02	.002	.04	–	.008	.04
NBS 37916	.0001	–	–	–	.05	.01	–	.002	.002	.02	–	.01	.15
NBS 37920	<.0001	–	–	–	.01	.002	–	–	–	.002	–	.01	–
NBS 37921	<.0001	–	–	–	.008	.002	–	.001	.002	.001	–	.005	–
NBS 37922	<.0001	–	–	–	.01	.005	–	.02	–?	.003	–	.01	.008
NBS 37923	<.0001	–	–	–	.01	.002	–	–	–	<.001	–	.01	–
Estimated limit of detection of these runs	<.0001	<.0002	.001	.005	.0002	<.0001	.0005	.0005	.001	.0005	.001	–	.005

Note: Values are as weight percent metallic element in freeze-dried sample; –, not detected; <, less than; >, greater than, not measured quantitatively.

All of the samples were examined by nondestructive neutron activation analysis for the selected elements, mercury, arsenic, copper, manganese, and vanadium. The samples were sealed in medical grade polyethylene vials, packed in a hexagonal array with a 1 ml water standard in the center, and irradiated for 1 minute. The samples were then allowed to decay for 3 days to reduce the activity of sodium-24. The samples were then transferred to a 4 dram preweighed polyvial, weighed, and counted for 15 minutes on a 60 cc GeLi detector. Comparisons were made with the standard solution to provide the semi-quantitative results given in Table 4.

The results given in Table 2, Table 3, and Table 4 are in qualitative agreement and are also in quantitative agreement consistent with the analytical uncertainties and evident inhomogeneity of the materials.

On the basis of these analyses, samples identified by the NBS numbers 37914, 37915, 37916, 37920, 37922, 37933, 37934, and 37935 respectively, were considered to be representative and were used in the equilibration experiments.

Table 4. Determination of Selected Elements in Bottom Materials by NAA

Sample No.	Mercury	Vanadium	Manganese	Arsenic	Copper
			Percent		
37913	.035	.0054	.14	1.1	.16
37914	.11	.0021	.04	.28	.13
37915	<.00005	.0050	.07	.0023	.008
37916	.0009	<.0010	.04	.0024	.018
37917	<.00006	.011	.11	.0039	.013
37918	.0002	.012	.09	.0015	
37919	.0006	.008	.11	.0033	.028
37920	<.00005	.010	.09	<.0002	.009
37921	<.00008	<.001	.21	.0015	
37922	.022	.011	.02	<.0004	
37923	<.00007	.009	.09	.0010	
37933	<.0001			.0013	.023
37934	.0002			<.0004	.013
37935	.0002			.0011	.014
37936	.0003			<.0003	.010

SECTION V

EQUILIBRATION PROCEUDRE

Selected samples of the bottom materials were equilibrated with water and with water containing NTA for study of possible chelation. Approximately 50 ml of the moist material was removed from the containers in several increments in order to obtain a representative sample and transferred to 500 ml polyethylene jars. Approximately 450 ml of distilled water or water containing NTA were added to each jar.

The NTA, Eastman Lot 701, was said to have a minimum assay of 97 percent by titration. It was used without further purification. Eighty milligram quantities were weighed, dissolved in 4 liters of distilled water, and used as the 20 ppm equilibrating solution.

The original intention was to adjust the pH of the water in the jars so that equilibrations would be made at pH values of 5.0, 7.0, and 9.0, respectively. However, this proved to be infeasible. The bottom material was found to have considerable buffer capacity so that large amounts of acid, or alkali were required to adjust to the desired pH values. Also the rate of approach to pH equilibrium was frequently slow and departures from the adjusted pH values often occurred during the equilibration process. It was also quite evident that the addition especially of acid but also of base to produce changes in pH could itself produce abnormal solubility effects. Accordingly, most of the equilibrations were made at the natural pH values related to the particular bottom material used.

The equilibrations were made by shaking the material with water, using a heavy-duty, box-type mechanical shaker. Shaking was continued for at least three hours at room temperature (25.0 ° ± 0.2 °C), after which the samples were allowed to settle for at least 16 hours.

Because the solutions were always cloudy, the supernatant liquid was decanted into clean certrifuge tubes and centrifuged at 2000 rpm (800 g) for 30 minutes, after which it was transferred to 125 ml glass-stoppered erlenmeyer flasks.

Sample 37922 would not clarify under the above described conditions. Accordingly, it was necessary to use a super-centrifuge which had a capacity of 16 tubes, each of 3 ml volume. At 7,000 rpm (6000 g) the supernatant liquid appeared to be essentially clear.

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SECTION VI

ANALYTICAL METHODS

Three analytical methods, atomic absorption spectroscopy (AAS), isotope-dilution solid-source mass spectrometry (IDMS), and neutron activation analysis (NAA) were used to analyze the equilibrated solutions. The objective was to investigate a large number of ions for possible solubility influences, rather than to obtain highly accurate data on a limited number of ions. Accordingly, semi-quantitative measurements were made which would give relative information in each specific case. The details of each method are described in the following sections.

A. Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry was used to determine the concentrations of nine elements (calcium, cadmium, copper, mercury, magnesium, manganese, nickel, lead, and tin) in the equilibrated solutions [1,2]. The instrument used was a Perkin-Elmer Model 403 with a premixed laminar flow burner for either an air-acetylene or nitrous oxide-acetylene burner head. This instrument is equipped with a deuterium arc lamp for background correction. However, the total solids in the solutions were low and background corrections were not necessary. The analytical conditions used for the measurements are given in Table 5.

Table 5. Analytical Conditions for the Determination of Trace Elements by AAS

Element	Wave Length °A	Hollow Cathode Lamp, Current mA[a]	Scale Expansion Factor	Range of Calibration Curve μg/ml
Ca	4227	20	1.0	1.0 – 10.0
Cd	2288	8	2.5	0.1 – 1.0
Cu	3247	15	7.0	0.1 – 1.0
Hg[b]	2537	6	--	0.001 – 0.04
Mg	2852	15	--	2.0 – 10.0
Mn	2795	20	5	0.1 – 1.0
Ni	2320	15	10	0.1 – 1.0
Pb	2833	6	5.0	0.2 – 1.0
Zn	2138	12	6.0	0.1 – 1.0

[a] Westinghouse HCl were used for all elements except for Cu
[b] Flameless atomic absorption spectrometry

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Equilibrated water samples were analyzed without pretreatment. Several of the solutions were cloudy and solids were observed to settle out on standing. No attempt was made to redisperse the solids. Rather, portions of the supernatant were withdrawn with a pipette, for analysis.

In natural water there are relatively few interferences encountered by atomic absorption spectrometry. Phosphate and sulfate are known to interfere in the determination of calcium and magnesium, however, under the test conditions, these anions either did not extract or were so low in concentration that no interferences were observed. As a check against possible interferences the standard addition method was used for each element. In this method a known concentration of the analyte is added to each test solution and the recovery determined by comparison with a calibration curve which was prepared in water free of interfering ions.

Standard stock solutions of each individual element were prepared from high purity metals or salts. Then, an appropriate dilution was made and a calibration curve was prepared for each element using the most sensitive ground state resonance line. The unknown solutions were aspirated into the flame and the absorbance measured for each element. To check the calibration curve, standard solutions were aspirated at frequent intervals during the determinations of the unknown solutions. Then, the concentrations of the unknown solutions were determined using a calibration curve prepared by means of a desk computer.

Mercury was determined by flameless atomic absorption using a modification of the procedure developed by Hatch and Ott [3]. The test portion was transferred to a reducing cell and diluted to 50 ml with a mixture of HNO_3 and H_2SO_4. The mercury was reduced to the free metal with hydroxylamine hydrochloride and stannous chloride. Then, the mercury was flushed from the reduction cell with a flow of argon into a heated absorption cell and the absorption measured at 2537 Å. To correct for light scatter or molecular absorption, the samples were repeated using a non absorbing line of tungsten at 2551 Å. Also, the standard addition method was used to check for possible losses in the method.

The precision obtained for Cd, Ni, Ca, Cu, Mg, Zn, Pb, and Mn by AAS was from 2-4 percent. However, the precision of the flameless technique for mercury was 10 percent.

B. Isotope-Dilution Spark-Source Mass Spectrometry (IDMS)

In an isotope dilution method, the concentration of an element in a matrix is determined from the change produced in its natural isotopic composition by the addition of a known quantity of the same element, the isotopic composition of which has been artificially altered. The concentrations are computed from:

$$C = \frac{W\,K\,(A_{sp} - B_{sp}\,R)}{M\,(BR - A)}$$

where C is the concentration in ppm (μg/g), W is the weight of isotopically enriched material ("spike") added in μg, M is the weight of sample in g, A and B are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundance of isotopes a and b in the spike, R is the measured altered ratio of isotope a to isotope b, and K is the ratio of the natural atomic weight to the atomic weight of the spike.

Applications of isotope dilution techniques to spark source mass spectrometry for simultaneous, multi-element determinations in metals have been described [4,5,6].

Fourteen elements were determined by this technique, including silver, barium, cadmium, chromium, copper, iron, mercury, molybdenum, nickel, lead, antimony, tin, strontium, and zinc. Solutions of the enriched isotope materials were prepared for the elements to be determined. Chemically compatable solutions were combined and volumetric additions of these "multiple spike" solutions were introduced into volumetric flasks. The flasks were made to volume by adding portions of the water (0 ppm NTA) and 20 ppm NTA solutions that had been equilibrated with the sediments. Aliquots of these spiked samples were pipetted into small quartz flasks and 0.3 ml of a 1 to 1 nitric-perchloric acid mixture were added to each flask. The acids were of high-purity grade. After evaporating the solutions in a "Clean Environment Chamber" [4], the solutions were heated further to $HClO_4$ fumes. This step destroyed the NTA and equilibrated the analytes with the enriched isotope spikes. The residue was dissolved in distilled water and the resulting solution was transferred to a Teflon electrolysis cell. The isotopically altered trace elements were electrodeposited onto two high-purity gold wire cathodes connected in parallel. Two gold wires served as the anodes. The cathodes were sparked in the spark source mass spectrograph and the spectra were photographically recorded.

For the initial samples, it was found that the solutions had been "over spiked", that is, the concentrations of the trace elements were appreciably lower than anticipated. Consequently, to obtain suitable isotope ratios for measurement, aliquots of the spiked samples were diluted with known volumes of the sample solutions and the procedures were repeated. The results were computed from the isotope dilution equation given above except that the concentration was computed in micrograms per milliliter of solution. Method blank determinations were made under the same experimental conditions and using the same volumes of acids.

C. Neutron Activation Analysis (NAA)

Neutron activation analysis is a useful technique for the determination of minute quantities of many elements. Elemental Analyses are usually treated in one of two ways. The first envolves chemical separations of the product radioisotopes with each separated chemical species determined individually. This type of procedure gives maximum sensitivity with minimum interference. However, multi-element analyses are tedious. The second procedure envolves a minimum of chemical manipulation utilizing high resolution gamma ray spectroscopy to identify the individual radioactive species. This method is somewhat less sensitive but yeilds many more elements determined for a given expenditure of time. This type of analysis was reported by Gills *et al.* for the determination of trace elements in Glass [7].

The application of neutron activation analysis to the determination of trace elements in the aquatic environment has been described by Funk, Bhagat, and Filby [8].

Samples of river bottom sediments and NTA solutions equilibrated with sediment were analyzed using the latter technique to determine metal chelation effects. Mercury, cobalt, manganese, copper, and arsenic were reported. The analyses gave total elemental composition.

The procedure used was as follows: Samples consisting of 5 ml of solution were sealed in 5 dram polyethylene vials, irradiated for 30 minutes in the pool H-5 facility at a thermal neutron flux of 2×10^{13}. Cobalt wires were used as flux monitors. After irradiation, samples were transferred to beakers, weighed, and brought to 6 *N* with HCl. The solutions were passed through hydrated antimony pentoxide (HAP) to remove sodium-24, brought to 50 ml volume and counted on the 47 cc Ge(Li) detector. Samples were compared to solution standards made by dissolving the metal or metal oxide and diluting to a known volume. Standards were treated in a like manner to that of the samples.

SECTION VII

RESULTS

The results of determinations of the concentrations of selected elements in the equilibrated solutions are given in Table 6 to Table 12. Altogether, 18 elements were determined. Copper and mercury were determined by all three techniques. Nickel, zinc, manganese, cadmium, and lead were determined by two techniques, while the remainder were determined by a single analytical competence.

In each table, the first column gives the sample number while the second lists the pH of the equilibrated solutions. Asterisks are used to indicate thy natural pH of the equilibrated solutions, while the other values were obtained by adjustment of pH by addition of acid or base during the equilibration procedure as already described. It is believed that only the starred values have significance as far as natural processes are concerned. However, the other data are presented for whatever interest they may have.

All analytically determined concentrations were expressed in parts-per-million ($\mu g\ cm^{-3}$). The concentrations of NTA in the solutions with which the materials were equilibrated are likewise given in parts-per-million. The analytical techniques used are identified as follows: AAS - atomic absorbtion spectroscopy; IDMS - isotope-dilution spark-source mass spectrometry; NAA - neutron activation analysis.

In addition to the tabulated data, several additional elements were determined in specific samples. Thus, lanthanum was found at low levels in several of the equilibrates but showed no correlation with the presence of NTA. Bromine was observed in relatively high concentrations of mercury, which may be an interesting observation.

The analytical values obtained by the several techniques are generally consistent, considering that semi-quantitative measurements were made. Also, there are no doubt some differences caused by inhomogeneity of the bottom materials, and to a lesser extent by equilibration problems. Nevertheless, the large number of equilibrated solutions analyzed minimizes the chance of faulty conclusions and the satisfactory agreement where multiple techniques were used lends confidence to those measurements where only one technique was employed.

Table 6. Determination of Copper and Mercury in Equilibrates

Sample No.	pH	0 ppm NTA AAS ppm	0 ppm NTA NAA ppm	0 ppm NTA IDMS ppm	20 ppm NTA AAS ppm	20 ppm NTA NAA ppm	20 ppm NTA IDMS ppm
				COPPER			
37914	7.0		.039			.039	
37914	9.0*	.036	.036	.02	.035	.034	.02
37915	5.0	.037			.099		
37915	7.0*		.012	.04		.023	.02
37915	9.0	.12	.074		.19	.26	
37916	8.2*	.019	.060	.04	.017	.034	.02
37920	7.9*	.017	.026		.075	.089	
37922	7.0		.030	.03		.032	.03
37922	9.0*	.26	.175		.29	.234	
37933	7.0*	.031	.033		.037	.044	
37933	9.0	.24	.173		.28	.190	
37934	7.0*	.010	.046	.02	.024	.053	.02
37935	7.7*	.009	.026	.02	.042	.048	.03
B	5.0		.028				
B	7.0					.008	
B	9.0					.029	
				MERCURY			
37914	7.0		.0019			.0019	
37914	9.0*		<.0015	<.01		<.0015	<.01
37915	7.0*		<.001	.1		<.001	.1
37915	9.0	<.0005	<.0017		<.0005	<.0016	
37916	8.2*	<.0005	<.001	.03	<.0005	<.001	.01
37920	7.9*	<.0005	<.001		<.0005	<.002	
37922	7.0		.89	.2		.85	.2
37922	9.0*	.016	1.00		.007	1.07	
37933	7.0*	<.0005	<.001		<.0005	<.002	
37933	9.0	<.0005	<.001		<.0005	<.001	
37934	7.0*	<.0005	<.004	.2	<.0005	<.004	.2
37934	9.0	<.0005	<.004	.01	<.0005	<.004	.01
37935	7.7*	<.0005	<.0005	.01	<.0005	<.0005	<.01
B	9.0					.006	

Table 7. Determination of Lead and Cadmium Equilibrates by AAS and IDMS

Sample No.	pH	0 ppm NTA		20 ppm NTA	
		AAS	IDMS	AAS	IDMS
			LEAD		
37914	9.0*	.08	.06	<.05	.04
37915	5.0	<.05		<.05	
37915	7.0*		.03		.08
37915	9.0	.14		.12	
37916	8.2*	.20	.09	.20	.06
37920	7.9*	<.05		<.05	
37922	9.0*	.18		.32	
37933	7.0*	<.05		<.05	
37933	9.0	.11		.15	
37934	7.0*	.17	.2	.15	.1
37934	9.0	<.05	.11	<.05	.12
37935	7.7*	<.05	.1	<.05	.2
			CADMIUM		
37914	9.0*	.028	<.001	.031	<.001
37915	5.0	.026		.030	
37915	7.0*		.002		.007
37915	9.0	.024		.023	
37916	8.2*		.001		.001
37922	7.0		<.001		<.005
37922	9.0*	.029		.029	
37933	9.0	.028		.024	
37934	7.0*		<.005		
37934	9.0	.027	.001	.027	.002
37935	7.7*		.002		.002

Table 8 Determination of Nickel and Zinc in Equilibrates by AAS and IDMS

Sample No.	pH	0 ppm NTA		20 ppm NTA	
		AAS	IDMS	AAS	IDMS
			NICKEL		
37914	9.0*	.02	.01, .03	.01	.01, .04
37915	5.0*	.04		.11	
37915	7.0		.01		.2
37915	9.0	.04		.14	
37916	8.2*	.02	.06	.15	.15
37920	7.9*	<.01		.02	
37922	9.0*	.05		.14	
37933	7.0*	.05		.15	
37933	9.0	.11		.05	
37934	7.0*	.04	.01	.07	.08
37934	9.0	<.01		.02	
37935	7.7*	.02	.04	.14	.15
			ZINC		
37914	9.0*	.002	.02, .03	.003	.004, .02
37915	5.0	.23		.42	
37915	7.0*		.02		.1
37915	9.0	.39		.53	
37916	8.2*	.067	.05	.090	.07
37920	7.9*	.010		.046	
37922	7.0		.03		.04
37922	9.0*	.30		.52	
37933	7.0*	.030		.070	
			CADMIUM		
37933	9.0	.23		.31	
37934	7.0*	<.001	.08	.022	.05
37934	9.0	.01	.06	.01	.07
37935	7.7*	<.001	.08	.41	.5

Table 9. Determination of Manganese in Equilibrates by AAS and NNA

Sample No.	pH	0 ppm NTA		20 ppm NTA	
		AAS	NAA	AAS	NAA
			MANGANESE		
37914	7.0		.002		.015
37914	9.0*	<.005	.006	<.005	.010
37915	5.0	26		>50	
37915	7.0*		.022		.439
37915	9.0	.48	.56	.55	.79
37916	8.2*	.06	.028	<.005	.041
37920	7.9*	.06	.041	.24	.148
37922	7.0		.010		.103
37922	9.0	.08	.199	.12	.378
37933	7.0*	.39	.455	.65	.765
37933	9.0*	.43	.492	.43	.800
37934	7.0*	.03	.004	.01	.001
37934	9.0	.05	.008	<.005	.002
37935	7.7*	<.005	.0005	<.005	.0011
B	7.0				.0008
B	9.0		.0008		

Table 10. Determination of Barium, Antimony, Molybdenum, Strontium, Chromium, Silver, Tin, and Iron in Equilibrates by IDMS

Sample No.	pH	NTA Concentration 0 ppm	20 ppm
		BARIUM	
37914	9.0*	.06	.06
37915	7.0*	.07	0.1
37922	7.0	<.1	<.1
37934	7.0*	<.03	<.03
37934	9.0		.04
37935	7.7*	0.2	
		IRON	
37914	9.0*	0.3	0.6
37915	7.0*	0.5	0.5
37916	8.2*	4	2
37922	7.0	1	1
37934	7.0*	1.4	1.5
37934	9.0	1	1
37935	7.7*	2	1
		MOLYBDENUM	
37914	9.0*	0.2	0.2
37916	8.2*	.05	.03
37922	7.0	.03	
37934	7.0*		<.004
37934	9.0	<.003	.006
37935	7.7*	.003	.002
		STRONTIUM	
37914	9.0*	1.2	1.2
37915	7.0*	0.3	0.4
37922	7.0	.02	.09
37934	7.0*	.2	.2
37934	9.0	.3	.3

Sample No.	pH	NTA Concentration 0 ppm	20 ppm
		CHROMIUM	
37914	9.0*		0.2
37915	7.0*	0.04	.05
37916	8.2*	.1	.1
37922	7.0	.03	.3
37934	7.0*	.02	.006
37935	7.7*	.1	.1
		SILVER	
37914	9.0*	<.001	<.001
37915	7.0*	<.002	<.001
37916	8.2*	.006	.001
37922	7.0	<.001	<.001
37934	9.4	<.001	<.001
37935	7.0	<.001	
37935	7.7*	<.001	<.001
		TIN	
37914	9.0*	.002	.002
37915	7.0*	<.01	<.01
37916	8.2*	.02	.003
37922	7.0	<.004	<.004
37934	7.0*	<.002	
37934	9.0	.002	.001
37935	7.7*	<.001	<.001
		ANTIMONY	
37914	9.0*	.004	.003
37916	8.2*	.004	.004
37934	9.0	.001	.001
37935	7.7*	.001	.001

Table 11. Determination of Calcium and Magnesium in Equilibrates by AAS

Sample No.	pH	NTA Concentrations 0 ppm	20 ppm
		CALCIUM	
37914	9.0*	147.	163.
37915	5.0	166.	209.
37915	9.0	2.4	3.9
37916	8.2*	2.1	3.2
37920	7.9*	.36	.68
37922	9.0*	2.5	3.2
37933	7.0*	17.	15.
37933	9.0	3.9	2.9
37934	7.0*	59.	49.
37934	9.0	24.	29.
37935	7.7*	28.	40.
		MAGNESIUM	
37914	9.0*	62.	54.
37915	5.0	22.	26.
37915	9.0	5.	5.
37916	8.2*	6.6	7.0
37920	7.9*	.6	1.3
37922	9.0*	7.	9.
37933	7.0*	3.8	3.6
37933	9.0	3.	5.
37934	7.0*	50.	39.
37934	9.0	24.	28.
37935	7.7*	6.4	8.7

Table 12. Determination of Cobalt in Equilibrates by NAA

Sample No.	pH	NTA Concentrations	
		0 ppm	20 ppm
37914	7.0	.34	.36
37914	9.0*	<.002	.005
37915	7.0*	.010	.041
37915	9.0	.023	.043
37916	8.2*	.024	.163
37920	7.9*	.004	.023
37922	7.0	.028	.083
37922	9.0*	.026	.058
37933	7.0*	.003	.046
37933	9.0	.030	.039
37934	7.0*	.054	.048
37934	9.0	.037	.030
37935	7.7*	.0005	.010
B	9.0	<.0005	.0005
B	5.0	.0005	

A study of the analytical data leads to the conclusion that residual concentrations of NTA have little or no effect upon the concentration of metal ions to be expected in bodies of water. No significant differences in concentrations of the following were found: barium, antimony, molybdenum, strontium, chromium, silver, tin, iron, lead, copper, and mercury. Significant but small increases were found for zinc and manganese in the solutions containing 20 ppm of NTA. However, in both cases, less than a two-fold increase was found and the maximum concentration was less than one part in a million. Cobalt was found to be solubilized by NTA but again the concentration was very small in that the highest concentration found was less than 0.2 ppm. The element nickel appears to be the most affected of all measured in that a three-fold increase in solubility was noted. However, the maximum concentration found amounted to only 0.15 ppm which is hardly a significant level.

An element of uncertainty in this work is the amount of NTA remaining at the conclusion of the equilibration procedure. In a natural situation an almost inexhaustible supply of residual NTA solution would be continuously available but this situation is difficult to reproduce in the laboratory. In the present experiments, it was only possible to equilibrate with a solution containing an initially determined level of NTA.

When the present experiments were undertaken, a reliable method for determination of residual concentrations of NTA was not available in this laboratory. After the work was completed and during the preparation of this report, an investigation of methods for NTA determination was initiated at NBS (Program No. 16020 GVY). A polarographic method under development in that investigation was used to determine the concentrations of NTA remaining in equilibrations similar to those reported here. These determinations showed that at least 15 to 50 percent of the initial NTA remained at the end of the equilibration procedure. Obviously, more work needs to be done to confirm the apparent degradation of the NTA and to understand the equilibria involved. However, it is evident that significant amounts of NTA remained throughout the equilibration experiments.

SECTION VIII

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SECTION IX

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